

Thermal isomerization of α -pinene in supercritical ethanol

A. Yermakova^b, A.M. Chibiryaev^a, I.V. Kozhevnikov^a, P.E. Mikenin^b, V.I. Anikeev^{b,*}

^a*Novosibirsk Institute of Organic Chemistry SB RAS, Pr. Acad. Lavrentieva 9, Novosibirsk 630090, Russia*

^b*Borisevsk Institute of Catalysis SB RAS, Pr. Acad. Lavrentieva 5, Novosibirsk 630090, Russia*

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Abstract

The experimental study followed by mathematical processing of the data showed that supercritical ethanol is an effective reaction medium for thermal isomerization of α -pinene. Rate of the reaction in supercritical solvent is by several orders of magnitude greater than the rate observed under normal conditions, with selectivity to the target reaction products being retained. The study allowed us for the first time to obtain the kinetic model of α -pinene isomerization in supercritical ethanol that takes into account temperature and pressure effect on the reaction rate and selectivity.

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1. Introduction

Studies on chemical reactions that proceed with participation of organic compounds in supercritical solvents-fluids (SCF) are performed to gain fundamental knowledge and provide serious practical applications. Due to special properties of substances in the critical region of their parameters, in some cases supercritical solvents lead to manifold increase in the chemical reaction rate and to controlled selectivity of the reaction (Jessop and Leitner, 1999).

Among supercritical solvents-fluids, water, CO₂, alcohols, and some saturated and unsaturated hydrocarbons are most suitable as a medium for chemical transformations. Supercritical water and CO₂ are regarded as most promising in terms of environmental safety. Besides, ethanol is also a common solvent widely used to conduct organic reactions under supercritical conditions; it is low toxic and benign to live objects. In combination with high solvation ability and respectively mild critical conditions (critical temperature $T_{cr} = 516.2$ K, pressure $P_{cr} = 63$ atm), ethanol finds an increasingly wide use as a supercritical fluid.

Among numerous reactions of organic compounds proceeding in supercritical fluids, of great practical importance are

transformations of phytogetic terpene compounds (α -pinene ($T_{cr} = 646.0$ K, $P_{cr} = 27.6$ atm), turpentine), since the products of such transformations (limonene, other monoterpene hydrocarbons) are applied in production of cosmetics and perfumery, polymeric and adhesive materials, domestic chemical goods. When thermal isomerization of α -pinene is conducted under normal conditions (without solvent) at 180–250 °C for the liquid-phase process (Fuguitt and Hawkins, 1945) or at 226–256 °C for the gas-phase processes (Gajewski and Hawkins, 1986), the 90–95% conversion of α -pinene can be attained at residence time varying from several hours to some days. This considerably restricts wide industrial application of such technology.

Main goals of the present work were experimental studies of thermal isomerization of α -pinene as a main component of turpentine in supercritical solvent and development of a kinetic model of the reaction based on experimental data. After preliminary study of some potential solvents (methanol, ethanol and 1-propanol), ethanol was chosen as the most friendly (ecologically clean) supercritical solvent.

2. Experimental

Experimental studies on thermal decomposition of terpene compounds in supercritical solvents were performed at the laboratory-scale setup (Anikeev et al., 2004) using a

* Corresponding author. Tel./fax: +7 383 339 7447.

E-mail address: anik@catalysis.nsk.su (V.I. Anikeev).

tubular flow-type reactor of volume ca. 14 cm³. Feed mixture was cooled at the reactor outlet, separated into gas and liquid phases, and analyzed. Composition of the reaction products in the liquid phase was determined by chromatomass-spectrometry using a gas chromatograph Hewlett-Packard 5890/II equipped with a quadrupole spectrometer HP MSD 5971 as a detector. Quartz column HP-5 (copolymer 5%-diphenyl-95%-dimethyloxane) of length 30 m, internal diameter 0.25 mm and stationary phase film thickness 0.25 μm were used for the analysis.

Temperature and pressure effects on conversion and selectivity of α -pinene isomerization in supercritical ethanol were studied in our experiments.

3. Development of the kinetic model

Two series of basic experimental data obtained on thermal isomerization of α -pinene in supercritical ethanol are presented in Table 1. The first series comprises the data on changes in the feed composition at temperature varying in the range of 560–660 K and constant pressure $P = 120$ atm. The second series of experiments shows effect of the feed pressure on the rate of α -pinene chemical transformations at constant temperature $T = 600$ K. The feed residence time was maintained constant and equal to 140 s in both series.

Commonly, the kinetic studies of complex reactions conducted in plug-flow reactors give the dependencies of feed composition on residence time under isothermal and isobaric conditions with a specified feed composition at the reactor inlet. The resulting “composition–residence time” integral curves are quite informative to postulate an assumed scheme of interconversion routes and to propose primary hypotheses about the form of kinetic functions intended for the description of individual reaction rates. The subsequent mathematical processing of experimental data allows determining the numerical values of constants in kinetic equations.

However, in some cases it seems more reasonable to obtain the dependences of feed composition on temperature and pressure at constant residence time. This approach was used

in our work to study thermal isomerization of α -pinene (Table 1). Note that processing of such data requires a mathematical model in which the number of constants (rate (preexponential) and activation energy constants) to be determined exceeds at least twofold the number of reaction routes. Since activation energies are the indices of exponential functions, this complicates parametric identification and may call into question reliability of the obtained parameters. Thus, solving of such a problem is accompanied with posterior verification of results for their statistical validity.

3.1. Kinetic model

Main routes of α -pinene isomerization in supercritical solvents can be presented as a scheme (Fig. 1) similar to the scheme of α -pinene thermal isomerization in the gas or liquid phase (Gajewski and Hawkins, 1986; Fuguitt and Hawkins, 1945). Reaction rates of each step are written as the first-order

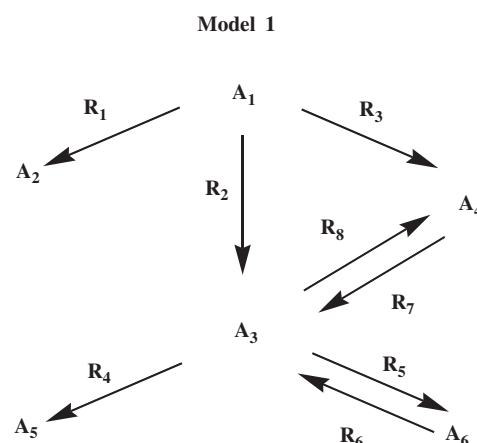


Fig. 1. Complete scheme of α -pinene thermal isomerization routes. A₁— α -pinene; A₂—limonene; A₃—alloocimene; A₄—neo-alloocimene; A₅— α - and β -pyronenes; A₆—others (products of alloocimene dimerization and polymerization, [4 + 2]-cycloaddition, etc.).

Table 1
The experimental data on thermal isomerization of α -pinene in supercritical ethanol

T (K)	P (atm)	The composition of reaction mixture normalized on the initial concentration of α -pinene (%)					
		α -pinene	Limonene	Alloocimene	Neo-alloocimene	(α + β) pyronene	Others
561	120	82.8	11.5	2.6	2.1	0.2	0.8
581		60.4	23.0	10.3	5.0	0.8	0.5
601		32.1	37.4	18.3	9.4	2.1	0.7
621		5.6	52.5	21.9	13.1	6.2	0.7
641		1.0	49.0	21.4	10.5	13.8	4.3
661		0.9	48.1	11.5	5.6	26.0	7.9
600	90	49.4	28.2	14.0	6.2	1.4	0.8
	120	32.1	37.4	18.3	9.4	2.1	0.7
	150	16.1	45.7	20.7	13.2	3.3	1.0
	180	10.4	48.3	24.2	12.2	4.2	0.7
	210	6.4	49.3	25.7	12.7	4.7	1.2
	270	3.3	52.2	20.3	16.5	5.7	2.0

kinetic equations:

$$\begin{aligned} R_1 &= k_1 C_1 & R_5 &= k_5 C_3 \\ R_2 &= k_2 C_1 & R_6 &= k_6 C_6 \\ R_3 &= k_3 C_1 & R_7 &= k_7 C_4 \\ R_4 &= k_4 C_3 & R_8 &= k_8 C_3 \end{aligned} \quad (1)$$

Concentration C of i th component of the mixture is shown as gmol/cm^3 , and constants as $1/\text{s}$. Each constant is presented as the Arrhenius function of temperature:

$$k_j(T, P_0) = k_{j0} \exp\left(\frac{-E_j}{RT}\right) \quad j = 1, 2, \dots, 8, \quad (2)$$

where E_j is the activation energy, J/mol , and R is the gas constant.

4. Mathematical description of experimental reactor

Mathematical model of a plug-flow reactor is represented by a set of ordinary differential equations:

$$\frac{dC_i}{d\tau} = \sum_{j=1}^{N_R} z_{ji} R_j \quad (3)$$

with initial conditions

$$\tau = 0: C_1 = C_1^0; C_i^0 = 0, \quad i = 2, \dots, N_S. \quad (4)$$

Here, C_i^0 denotes the inlet concentrations of components, $N_S=6$ is the number of components, $N_R=8$ is the number of chemical reactions involved in the conversion scheme under consideration (Fig. 1). Numbers z_{ji} designate j th row and i th column of a stoichiometric matrix corresponding to the reaction scheme accepted above. Residence time $\tau = V_R/Q_S$, V_R is the reactor volume (cm^3), and Q is the flow rate (cm^3/s).

Taking into account equivalent transformations by introduction of dimensionless concentrations $y_i = C_i/C_1^0$, set of equations (3) can be written as:

$$\frac{dy_i}{d\tau} = \sum_{j=1}^{N_R} z_{ji} R_j(y) \quad \tau = 0: y_1^0 = 1, y_i^0 = 0, \quad i = 2, \dots, N_S. \quad (5)$$

Set of equations (5) was used to identify the model parameters.

5. Model identification

The identification includes determination of unknown values of rate and activation energy constants that provide the best fit of experimental and calculated data. For this purpose, a target function is formulated, which should be minimized by parameters:

$$Q = \sum_{k=1}^{N_{\text{EXP}}} (\mathbf{y}_k^{\text{exp}} - \mathbf{y}_k^{\text{calc}}(\mathbf{p}))^T \mathbf{W}_k^{-1} (\mathbf{y}_k^{\text{exp}} - \mathbf{y}_k^{\text{calc}}(\mathbf{p})) \rightarrow \min(\mathbf{p}). \quad (6)$$

In formula (6), the following vector designations are accepted: $\mathbf{y}_k^{\text{exp}}$ is the N_S -dimensional column vector composed of experimentally measured concentrations of i th component in each k th experiment, and $\mathbf{y}_k^{\text{calc}}$ is the vector of calculated concentration values obtained by integration of a set of differential equations of model (5) within 0–140 s at the corresponding temperature T_k with regard to (1) and (2). \mathbf{p} denotes the N_P -dimensional column vector of desired parameters ($N_P = 16$):

$$\mathbf{p} = [k_1^0, k_2^0, \dots, k_8^0, E_1, E_2, \dots, E_8]. \quad (7)$$

Minimization (6) was performed by the classic Gauss–Marquardt iteration method (Marquardt, 1963). The calculated values of concentrations are found at each iteration step by numerical integration of system of differential equations (6) at current values of constants.

To calculate the admissible step and direction of advancing to the minimum point, this method applies the matrix of second-order derivatives of the target function with respect to parameters. In Gaussian approximation, matrix \mathbf{X} forms as (Bard, 1970):

$$\mathbf{X} = (\partial Q / \partial \mathbf{p})^T (\partial Q / \partial \mathbf{p}). \quad (8)$$

Vector of the target function derivatives with respect to parameters $\partial Q / \partial \mathbf{p}$ at each iteration step is calculated via numerical differentiation.

The iteration reduces matrix \mathbf{X} to the form of correlation matrices by normalization to $X_{i,i}^{1/2}$. However, division by $X_{i,i}^{1/2}$ is performed if $X_{i,i} > 10^{-3} \times \text{trace}(\mathbf{X})/N_P$. When matrix \mathbf{X} is ill conditioned and its inversion, aimed at obtaining the reciprocal matrix \mathbf{X}^{-1} necessary to calculate the next step, leads to significant errors, the regularization method should be used via introducing regularization parameter β . In this case, matrix $\mathbf{X} + (\beta) \times \mathbf{I}$, where \mathbf{I} is a unit matrix, is used instead of \mathbf{X} . With a properly chosen scalar factor β , the resulting matrix is well inverted. The developed program provides the algorithm for optimal selection of parameter β at each iteration. The normalized form of matrix \mathbf{X} allows using a simple algorithm to select parameter β by its variation over the scale 0, 10^{-6} , 10^{-5} , 10^{-4} , \dots , 1.

Note that for well conditioned problems, in the vicinity of the minimum point Q (Eq. (6)) the value of β tends to zero ($\beta \approx 10^{-6}$), which provides unbiased estimation of constants. Otherwise, after completion of the iteration process, the β value remains quite large ($\cong 10^{-2}$ and more), which indicates that the problem is ill conditioned and the biased estimation of constants is obtained. Therefore, numerical values of this parameter at iterations allow one to predict condition of the problem.

Ill condition of matrix \mathbf{X} is caused by excessive information in the model under consideration; for instance, redundant routes were introduced, i.e., the routes that may occur, but for some reason the experimental data obtained are insensitive to these routes. In such cases, the problem of reasonable simplification of the model arises. Simplification strategy is determined for each case by posterior analysis of the results. In our work, such analysis was performed by studying the properties

of the target function surface in the vicinity of the minimum point (the so-called ε -indifference region) (Bard, 1970), which virtually reduces to analyzing the spectrum of eigenvalues and eigenvectors of matrix \mathbf{X} (Vajda et al., 1986).

6. Selection of the reaction route model

Minimization of the target function (6) with the use of complete model based on the route scheme (Fig. 1) required more than 100 iteration steps. This gave a satisfactory result in terms of conformity between experimental and calculated data. Root-mean-square absolute error of discordance between these data comprised 1.6%. Note that analysis of various recommendations about selection of weight matrix \mathbf{W} in Eq. (6) (Valko and Vajda, 1987) provided the best result with the unit matrix $\mathbf{W}=\mathbf{I}$.

Detailed statistical information on the results is presented in Table 2, and Fig. 2 provides graphical illustration of agreement between experimental and calculated data. The data of Table 2 and the dependencies in Fig. 2 show that at exclusively good description of experimental data there are some parameters that are determined with high uncertainty. This is attested by their large confidence intervals corresponding to the 95% confidence level, which in some cases exceed several times the estimated values of constants. Among such parameters are rate constants of routes 2, 5, 6, 7 and 8, and their activation energy constants. The experimental data are apparently insensitive to the listed routes. Large confidence intervals directly indicate the confluence of matrix \mathbf{X} , whose eigenvalues are close to zero.

The analysis of experimental data shows that the ratio of concentrations of two alloocimene isomers (alloocimene and neo-alloocimene) in the reaction products is virtually similar at all temperatures and equal to ca. 2 (see Fig. 2). This value gives good estimation of equilibrium constant for steps 7 and 8, which appeared weakly dependent on temperature. Note that the alloocimene to neo-alloocimene reversible conversion proceeds much faster as compared to other products; hence, at all temperatures the state of these two products is close to thermodynamic equilibrium, and their ratio is determined by the equilibrium constant. This is why the constants of reversible steps 7 and 8 cannot be identified; thus, the model should be reduced: two indicated isomers are taken as a new component ($A_3 + A_4$), and their concentrations are summed up.

Route 6 in Fig. 1 can be neglected due to small value of rate constant k_6 . The identification process automatically rejects this route from the model. However, although rate constant of route 5 also appeared poorly determined, this route should be retained. Removal of reaction 5 may distort the physical meaning of the model, since this is the reaction that yields comparatively small amounts of various admixtures A_6 , such as products of alloocimene dimerization and polymerization, [4 + 2]-cycloaddition, and others.

The above reasoning allowed us to suggest a simplified reaction scheme shown in Fig. 3. Results of repeated identification are presented in Table 3. Thus, this scheme with constants listed in Table 3 is taken as a basis of kinetic model. Conformity of experimental and calculated data is illustrated by Fig. 4.

Table 2

Results and statistical information on the rate constants estimation calculated using a total model (Fig. 2)

Rate constants and confidence intervals ^a			
$k_{0,1}$	$7.054\text{E} + 07 \pm 2.008\text{E} + 07$	E_1	$1.176\text{E} + 05 \pm 1.270\text{E} + 04$
$k_{0,2}$	$8.344\text{E} + 01 \pm 1, 786\text{E} + 03$	E_2	$6.645\text{E} + 04 \pm 9.454\text{E} + 05$
$k_{0,3}$	$3.570\text{E} + 09 \pm 2.840\text{E} + 09$	E_3	$1.382\text{E} + 05 \pm 4.490\text{E} + 04$
$k_{0,4}$	$1.088\text{E} + 08 \pm 2.566\text{E} + 08$	E_4	$1.251\text{E} + 05 \pm 1.182\text{E} + 05$
$k_{0,5}$	$1.269\text{E} + 00 \pm 2.478\text{E} + 01$	E_5	$3.348\text{E} + 04 \pm 1.266\text{E} + 06$
$k_{0,6}$	$5.535\text{E} - 06 \pm 7.366\text{E} - 01$	E_6	$1.004\text{E} + 01 \pm 7.908\text{E} + 09$
$k_{0,7}$	$5.000\text{E} + 00 \pm 3.195\text{E} + 11$	E_7	$2.500\text{E} + 05 \pm 1.267\text{E} + 17$
$k_{0,8}$	$1.539\text{E} - 02 \pm 1.574\text{E} - 02$	E_8	$1.310\text{E} + 02 \pm 5.690\text{E} + 04$
Root-mean-square absolute error			1.13%

^a $[k_{0,i}]$ —1/s, $[E_i]$ —J/mole.

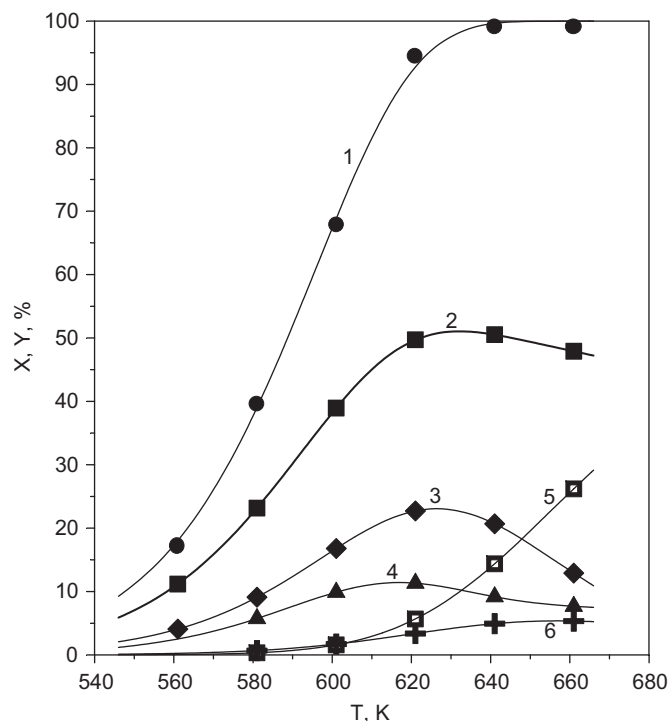


Fig. 2. α -pinene conversion and yield of products versus the temperature. Comparison of experimental and calculated data (the complete model). $P = 120$ atm. 1— α -pinene, 2—limonene, 3—alloocimene, 4—neo-alloocimene, 5—($\alpha + \beta$)-pyronenes, 6—others.

7. Pressure effect on the reaction rate constants

7.1. Mechanism of α -pinene isomerization in the context of transition state theory

As noted above, it was shown experimentally that the reaction rate is strongly dependent on total pressure in the system. In the general case, pressure effect on the rate constant reflects specific interaction of supercritical solvent and chemical components reacting in this solvent. In some cases, the

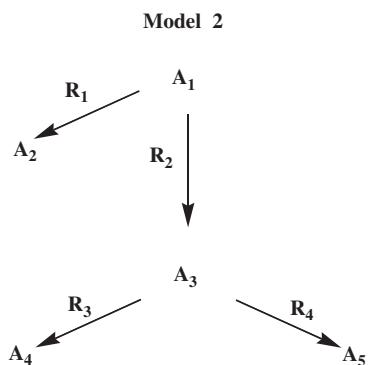


Fig. 3. The abbreviated scheme of α -pinene thermal isomerization routes. A_1 — α -pinene; A_2 —limonene; A_3 —alloocimene and neo-alloocimene; A_4 — α - and β -pyronenes; A_5 —others.

Table 3

Results and statistical information on the rate constants estimation calculated using a simplified model (Fig. 4)

Rate constants and confidence intervals ^a			
$k_{0,1}$	$8.505E+07 \pm 1.381E+07$	E_1	$1.180E+05 \pm 8.069E+03$
$k_{0,2}$	$2.727E+09 \pm 4.993E+08$	E_2	$1.366E+05 \pm 9.195E+03$
$k_{0,3}$	$1.083E+08 \pm 6.149E+07$	E_3	$1.294E+05 \pm 3.095E+04$
$k_{0,4}$	$1.229E+03 \pm 1.371E+03$	E_4	$7.425E+04 \pm 6.061E+04$
Root-mean-square absolute error		0.97%	

^a $[k_{0,i}]$ —1/s, $[E_i]$ —J/mole.

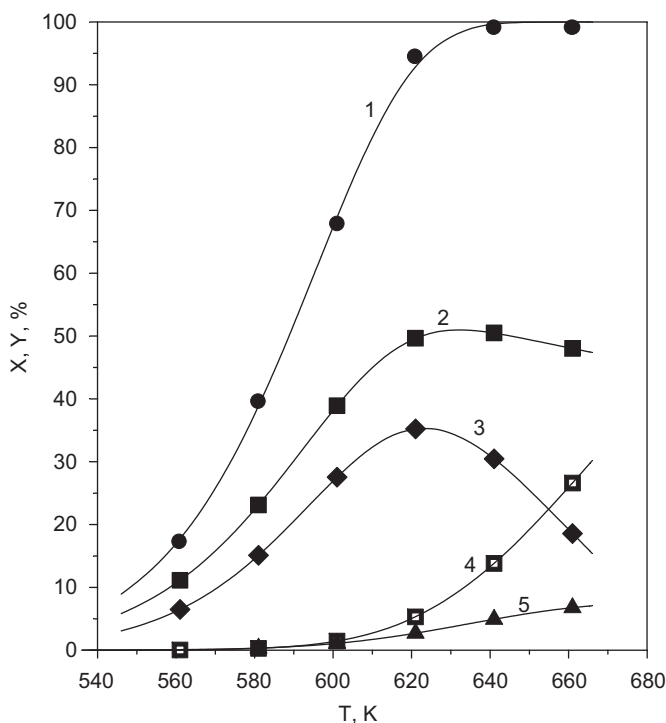
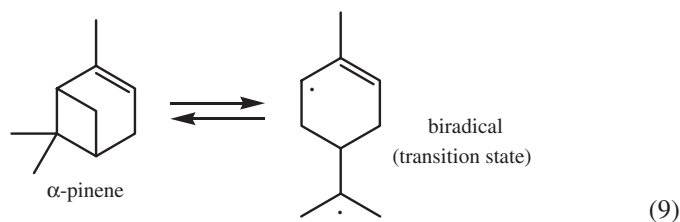


Fig. 4. α -pinene conversion and yield of products versus the temperature. Comparison of experimental and calculated data (the short scheme). 1— α -pinene, 2—limonene, 3—alloocimene and neo-alloocimene, 4—(α + β)-pyronenes, 5—others.

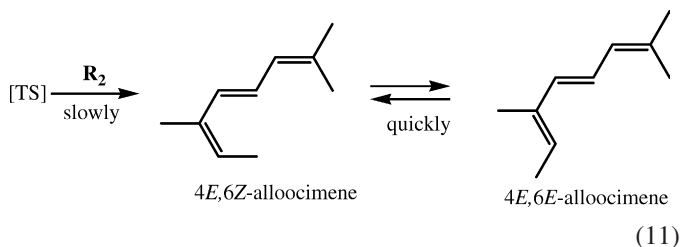
transition state theory is used for interpretation and quantitative description of the effect of solvent pressure (density) on the apparent rate constants of chemical reactions (Carey and Sundberg, 1977).

According to this theory, motion in the chemical reaction coordinate escapes the potential energy barrier, whose peak corresponds to potential energy of “activated complex” (Transition State (TS))—transition state of the molecule between its initial and final structure.

Within this theory, the initial and fast step of α -pinene transformation is the formation of TS; here it is a biradical, which is in equilibrium with the initial α -pinene, i.e.,



This is followed by supposedly irreversible decomposition of TS into the products by two routes:



The rates of reactions proceeding by steps (10) and (11) at reference temperature $T_0 = 600$ K, which was used in the experiments with varying pressure, are presented as:

$$R_1(T_0, P) = k_1(T_0, P)y^\#, \quad R_2(T_0, P) = k_2(T_0, P)y^\#, \quad (12)$$

where $y^\#$ is the concentration (dimensionless) (TS).

Equilibrium of step (9) is expressed by equation

$$-RT \ln K^\# + RT \ln(f_{TS}/f_{A_1}) = 0, \quad (13)$$

where $f_i = Py_i\Phi_i$ is the fugacity of i th component, $i = \text{TS}$, and A_1 is α -pinene. Fugacity coefficients $\Phi_i = \Phi_i(y, T, P)$ are in turn the functions of temperature, pressure, critical and other parameters of individual components and molar composition of the mixture.

If activated complex is taken as a certain real molecule, equilibrium constant $K^\#$ for this complex and reacting substance is expressed as a change of standard Gibbs energy ($\Delta G^\#$) using a well-known thermodynamic relation:

$$-\Delta G^\# = RT \ln K^\#. \quad (14)$$

Index # at ΔG relates to the change in Gibbs energy that accompanies the activation process, when initial substance and TS are taken at their standard (hypothetical) states. Ideal-gas state at the process temperature and unit pressure is selected as the standard state.

Subject to Eq. (13), TS concentration ($y^\#$) is found from the experimentally measured concentration of α -pinene using relation

$$y^\# = K^\# (\Phi_{A_1} / \Phi_{TS}) y_1. \quad (15)$$

Substituting (15) to Eqs. (12) gives

$$\begin{aligned} R_1(T_0, P) &= k_1(T_0, P_0) K^\# \frac{\Phi_{A_1}}{\Phi_{TS}} y_1, \\ R_2(T_0, P) &= k_2(T_0, P_0) K^\# \frac{\Phi_{A_1}}{\Phi_{TS}} y_1. \end{aligned} \quad (16)$$

Let us introduce designations:

$$\begin{aligned} k_{1app}(T_0, P) &= k_1(T_0, P_0) K^\# \frac{\Phi_{A_1}(T_0, P)}{\Phi_{TS}(T_0, P)}, \\ k_{2app}(T_0, P) &= k_2(T_0, P_0) K^\# \frac{\Phi_{A_1}(T_0, P)}{\Phi_{TS}(T_0, P)}, \end{aligned} \quad (17)$$

where k_{1app} and k_{2app} are the so-called “apparent” rate constants of steps (10) and (11). Numerical values of $k_1(T_0, P_0)$ and $k_2(T_0, P_0)$ at $T_0 = 600$ K and $P_0 = 120$ atm are obtained from formula (2) using the data of Table 3. Pressure effect on the apparent rate constants is expressed in Eqs. (17) by appropriate functions of fugacity coefficients.

It is known (Sandler, 1999) that partial derivatives of fugacity coefficient with respect to pressure at constant temperature and composition of the mixture are equal to partial molar volume (\bar{V}_i) of component, which gives

$$(\partial \ln \Phi_i / \partial P)_T = \bar{V}_i / RT. \quad (18)$$

Logarithmic differentiation of Eqs. (17) with substitution of (18) leads to equations of the following form:

$$\begin{aligned} \frac{\partial}{\partial P} \left(\ln \frac{k_{iapp}(T_0, P)}{k_i(T_0, P_0)} \right) &= \left(\frac{\partial \ln \Phi_{A_1}}{\partial P} - \frac{\partial \ln \Phi_{TS}}{\partial P} \right) \\ &= \frac{-\Delta \bar{V}^\#}{RT}, \quad i = 1, 2. \end{aligned} \quad (19)$$

Here the value $\Delta \bar{V}^\# = \bar{V}_{TS} - \bar{V}_{A_1}$, representing the difference of partial molar volumes of transition complex and reagent, is conventionally called the “activation volume”.

Numerical value of $\Delta \bar{V}^\#$ depends on both the internal properties of the system—properties of the reagent, and the external properties determined by the solvent. Note that the $\Delta \bar{V}^\#$ value can be either negative or positive.

Integrating (19) over an interval $P_0 - P$ ($P_0 = 120$ atm) gives the dependence of apparent rate constants of chemical reactions on pressure:

$$\begin{aligned} \ln k_{i,app}(T_0, P) &= \ln k_i(T_0, P_0) - \frac{1}{RT} \int_{P_0}^P \Delta \bar{V}^\#(P) dP, \\ i &= 1, 2. \end{aligned} \quad (20)$$

8. The problem of parameters identification using a series of data with alternating pressure

The lack of a simple explicit expression describing the dependence of $\Delta \bar{V}^\#(P)$ on P makes it difficult to use Eq. (20) when solving the inverse problem that consists in determination of apparent constants. However, on discrete intervals $P_1 - P_0, P_2 - P_0, \dots, P_k - P_0$ belonging to the range of pressure variation in the experiment, the mean-value theorem is applicable, and integrals in (20) can be represented as

$$\begin{aligned} \ln k_{i,app}(T_0, P_k) &= \ln k_i(T_0, P_0) - \frac{\Delta \bar{V}_k^\#}{RT} \int_{P_0}^{P_k} dP \\ &= \ln k_i(T_0, P_0) - \frac{\Delta \bar{V}_k^\#}{RT} (P_k - P_0). \end{aligned} \quad (21)$$

Here, $\Delta \bar{V}_k^\#$ is the mean integral of $\Delta \bar{V}^\#(P)$ on the pressure interval $P_k - P_0$. Evidently, this value is also the pressure function. A preliminary analysis of experimental data showed that the relationship between $\Delta \bar{V}_k^\#$ and P can be represented by the empirical equation:

$$\Delta \bar{V}^\# = b_0 + b_1 P + b_2 P^2. \quad (22)$$

Similar to the previous case, the inverse problem was solved using a simplified scheme of reaction routes (Fig. 3) by minimization of target function (6) and calculation of the concentrations via numerical integration of a set of equations (5). Subject to relationship (22), the constants were represented as

$$k_{i,app} = k_i(T_0, P_0) \exp \left(-\frac{\Delta \bar{V}^\#(P)}{RT} (P - P_0) \right). \quad (23)$$

Here, model parameters to be determined are the coefficients of Eq. (22), since preexponents $k_i(T_0, P_0)$ ($i = 1, 2$) were calculated by formula (2) using the previously found values of activation energies.

This gave the coefficients:

$$\begin{aligned} b_0 &= -1974.63 \pm 136.85, \\ b_1 &= 13.15 \pm 0.91, \\ b_2 &= -0.022 \pm 0.002. \end{aligned} \quad (24)$$

Thus, the pressure effect is taken into account only for two rate constants corresponding to routes 1 and 2 in scheme 3. However, this effect certainly impacts on the concentrations of component A_3 (the sum of alloocimene and neo-alloocimene), which in turn determines the yield of A_4 (the sum of pyronenes) and A_5 (other by-products).

The calculated value of $\Delta \bar{V}^\#$ on the interval of pressures under consideration is negative; hence, the rate constants grow with pressure increase. The conformity of experimental and calculated data is shown in Fig. 5. The largest gradient of the constants' growth is observed in the pressure range of 90–120 atm, which is close to the ethanol critical pressure. As pressure increases, this gradient diminishes; and in the range of 210–270 atm pressure effect on the constants becomes less pronounced.

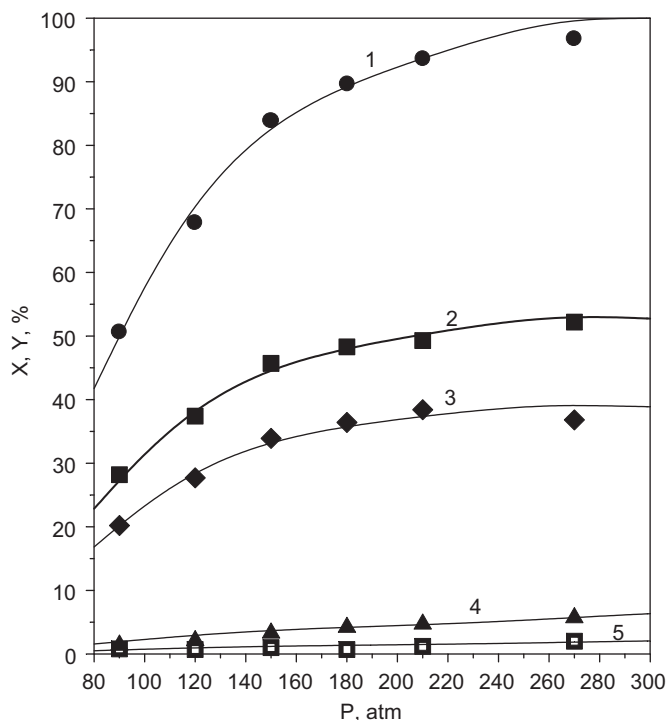


Fig. 5. α -pinene conversion and yield of products versus the pressure. Comparison of experimental and calculated data. 1— α -pinene, 2—limonene, 3—alloocimene + neo-alloocimene, 4— $(\alpha + \beta)$ -pyronenes, 5—others.

To summarize this section, it can be stated that an adequate kinetic model of α -pinene thermal isomerization in supercritical ethanol has been developed; this model holds true for temperature range 562–660 K and pressure range 90–270 atm.

9. Results and discussion

9.1. Reaction rate

Compared to the liquid- or gas-phase variants of α -pinene thermal isomerization (Fuguitt and Hawkins, 1945; Gajewski and Hawkins, 1986), supercritical ethanol provides a sharp increase in the reaction rate over all routes: high degree of α -pinene conversion is attained already in 140 s. It was demonstrated that the reaction rate can be effectively controlled by changing not only the temperature, but also the pressure, which is typical of the reactions in supercritical solvents (Anikeev and Yermakova, 2003; Anikeev et al., 2004).

9.2. Reaction selectivity

A simplified scheme of reaction routes and the results on selectivity of transformations are in good agreement with the literature data on thermal isomerization of α -pinene under normal conditions in both the liquid and gas phases (Fuguitt and Hawkins, 1945; Gajewski and Hawkins, 1986). Fig. 6 displays the reaction selectivity versus the yield of main reaction products. The selectivity is determined as an integral quantity: a ratio of the product yield to α -pinene converted under the given conditions.

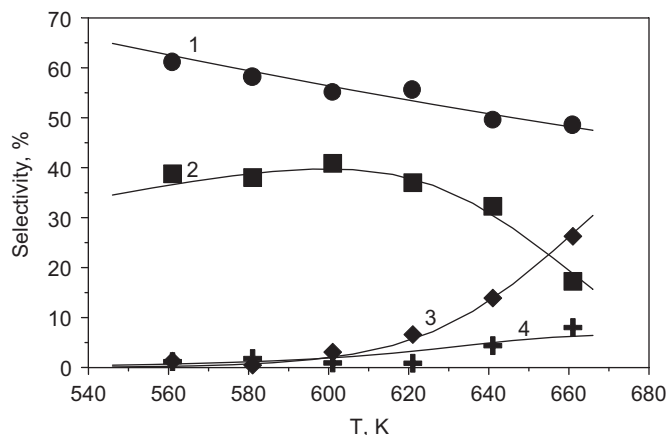


Fig. 6. The temperature dependence of the reaction selectivity. 1—limonene, 2—alloocimene + neo-alloocimene, 3— $(\alpha + \beta)$ -pyronenes, 4—others.

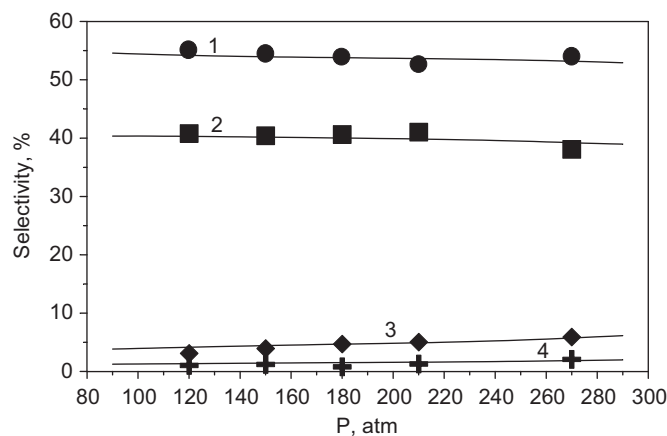


Fig. 7. The pressure dependence of the reaction selectivity. 1—limonene, 2—alloocimene + neo-alloocimene, 3— $(\alpha + \beta)$ -pyronenes, 4—others.

It follows from Fig. 6 that the main product of α -pinene thermal isomerization in supercritical ethanol is limonene. The yield of this products attains 50–60%; however, it slightly decreases at temperature elevation. Selectivity of the reaction to limonene is expressed as the ratio of rate constants:

$$S_{Li} = \frac{k_{10} \exp(-E_1/RT)}{k_{10} \exp(-E_1/RT) + k_{20} \exp(-E_2/RT)}. \quad (25)$$

Since $E_2 > E_1$, a slight decrease in selectivity is observed with increasing temperature. Accordingly, the elevated temperature strengthens route 2 (scheme in Fig. 3), which gives an increased yield of alloocimene isomers. However, a further temperature increase in the reaction sequences $A_1 \rightarrow A_3 \rightarrow A_4$ and $A_1 \rightarrow A_3 \rightarrow A_5$ makes predominant the rates that lead to A_4 (the sum of pyronenes) and A_5 (other by-products). Therefore, at further temperature elevation, selectivity to intermediate product A_3 decreases due to increased yield of α - and β -pyronenes and A_5 products.

Pressure effect on the reaction selectivity is illustrated by plots in Fig. 7, which indicate that pressure exerts no significant effect on the reaction selectivity. This agrees with the above model, since the ratio of constants $k_1(T, P)/k_2(T, P)$ does not

change with pressure growth. Only the increased reaction rates are observed by lines $A_1 \rightarrow A_2$ and $A_1 \rightarrow A_3$.

10. Conclusion

The experimental study followed by mathematical processing of the data showed that supercritical ethanol is an effective reaction medium for thermal isomerization of α -pinene. Rate of the reaction in supercritical solvent is by several orders of magnitude greater than the rate observed under normal conditions, with selectivity to the target reaction products being retained.

The study allowed us for the first time to obtain the kinetic model of α -pinene isomerization in supercritical ethanol that takes into account temperature and pressure effect on the reaction rate and selectivity.

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